

II. GROUNDWATER CHEMISTRY MODEL

A. INTRODUCTION

Variations in the chemistry of groundwater can have a significant impact on the transport behavior of radionuclides. For example, the solubility and sorption behavior of the various radionuclides of interest are a function of groundwater chemistry. To derive bounds on transport parameter values pertaining to the post-closure period of the potential repository, experiments must be carried out as a function of groundwater chemistry.

A groundwater chemistry “model” has been developed that can be used to bound the potential variations in groundwater chemistry to be expected in the post-closure period. This model consists of a set of conceptual submodels that describe the chemical processes that control the chemical evolution of pore waters, perched waters, and groundwaters in Yucca Mountain.

Experiments are used to quantify the submodels, and the results of the experiments can be used to link the submodels using variations in water chemistry observed in the site-characterization phase of this project to calibrate the resulting linked models. Unfortunately, the experimentation phase of the project was not carried to completion as a result of budget constraints. As a result, the linking of the conceptual models remains incomplete.

Purpose and Scope

The purpose of the Groundwater Chemistry Modeling Task is to develop models that describe compositional variations in groundwaters in the unsaturated and saturated zones beneath Yucca Mountain. These models will be used to establish bounds on the water compositions to be expected in the ambient Yucca Mountain flow system. They will also be used to bound the composition of waters in the far field of the potential repository at Yucca Mountain in the post-closure period. This information will be used by various other tasks in

the project.

In this chapter, we will review the currently available data on the chemistry of waters in Yucca Mountain and develop and discuss models that explain the observed variations. We will combine 1) analytical data for precipitation (rain and snow), for pore waters and perched waters from the unsaturated zone at Yucca Mountain, and for groundwaters from the saturated zone at Yucca Mountain, 2) experimental and theoretical data and models for soil-water and rock-water interactions, and 3) computer modeling to identify both the controls on unsaturated-zone and saturated-zone water compositions in Yucca Mountain and the ranges in chemical compositions to be expected in these waters over the lifetime of the proposed repository.

Computer modeling with the code EQ3/6 was used as a tool to formulate and test conceptual models. However, its use in the prediction of future variations in water compositions is severely restricted because appropriate data on the identity of secondary (alteration) phases and data on the kinetics of formation of these phases (nucleation and crystallization) are lacking. For this reason, only preliminary work has been accomplished, and our discussion in this report does not include extensive reference to EQ3/6 modeling results.

B. GROUNDWATER CHEMISTRY

Sources of Data

The main sources of data for this chapter are the publications on precipitation compositions by McKinley and Oliver (1994, 1995) and publications on groundwater chemistry by Ogard and Kerrisk (1984) and Yang et al. (1988, 1996). It is important to state that the groundwater chemistry data of Ogard and Kerrisk and of Yang et al. represent samples from a very limited number of sites and may not be fully representative of waters in the overall Yucca Mountain flow system.

Precipitation Compositions

Precipitation compositions are important for modeling the compositions of waters at Yucca Mountain because they represent the starting point in the evolution of groundwater chemistry. Precipitation compositions are commonly separated into wet-fall and dry-fall. The composition of wet-fall reflects those solutes in falling rain or snow. The composition of dry-fall reflects the dust composition deposited on the land surface. The composition of wet-fall varies with geographic position due to numerous factors, such as the distance of the sampling site from the ocean (Wagner and Steele 1989). An approximation of wet-fall compositions at a given site can best be obtained by sampling while rain or snow is falling. Dry-fall compositions can be obtained by sampling dust.

A common approach to measuring precipitation compositions is to sample rain gauges and rain collectors either on a regular basis or after significant precipitation events. The precipitation compositions obtained with this approach reflect wet-fall, soluble dry-fall, and evaporation that occurred prior to removal of the sample from the collector. These compositions will here be called integrated precipitation compositions, or simply, precipitation compositions.

Dust (dry-fall) compositions were reported for

southern Nevada and the Yucca Mountain area by Reheis et al. (1995). Separate analyses of wet-fall are not available for the Yucca Mountain area, and only a limited number of analyses of integrated precipitation samples is available (Stezenbach 1992). Fortunately, an excellent database of integrated precipitation compositions for the Nevada Test Site area has been provided by a sampling network established by the U. S. Geological Survey in the Kawich Range just north of the Nevada Test Site (McKinley and Oliver 1994, 1995). This database will be used extensively in this report.

Average concentrations for the major constituents in integrated precipitation samples from the Kawich Range site are given in Table 7.

As an example of the variability in precipitation compositions, data for sulfate and chloride concentrations in integrated precipitation samples from the Kawich Range sites are plotted in Fig. 10. The observed scatter reflects variations in wet- and dry-fall compositions between sampling events, variations in the relative contributions from wet-fall and

Table 7. Average Integrated Precipitation Composition at Kawich Range Sites*

Component	Concentration (mg/l)
SiO ₂	0.17
Calcium	0.96
Magnesium	0.11
Sodium	0.64
Potassium	0.24
Manganese	0.0084
Strontium	0.0058
Chloride	0.55
Fluoride	0.02
Sulfate	1.18
Nitrate	0.42
Alkalinity	2.7
pH	6.1

*from McKinley and Oliver (1994, 1995)

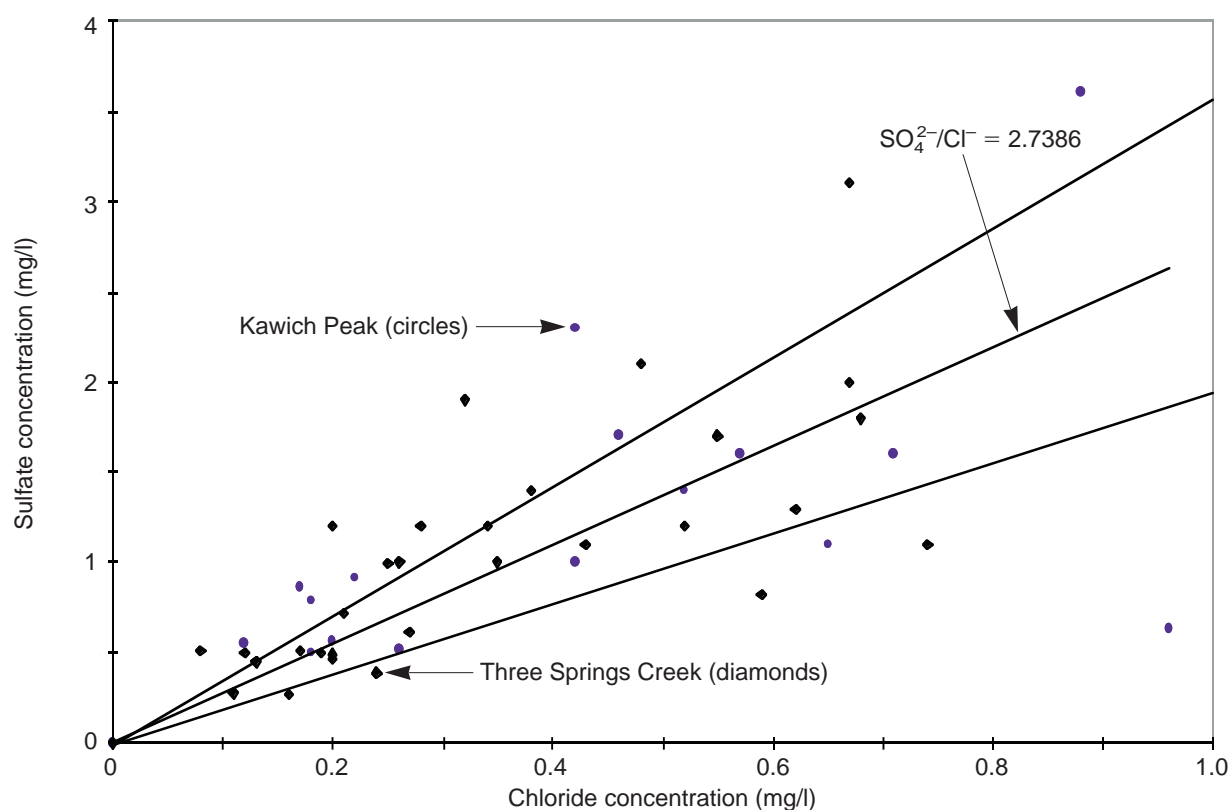


Figure 10. Sulfate versus Chloride in Precipitation. Concentrations of sulfate are plotted against concentrations of chloride for integrated precipitation samples from the Kawich Range sites (from McKinley and Oliver 1994, 1995). The slope of the inner line (a regression fit) gives the $\text{SO}_4^{2-}/\text{Cl}^-$ ratio of the points plotted. The two outer lines represent a standard deviation of one sigma from the regression line.

dry-fall in any given sample, evaporation, and analytical errors. Only samples with less than 1.0 mg/l were plotted. Samples with higher chloride concentrations showed significantly greater variability in chloride-to-sulfate ratios, suggestive of unusually high dust inputs. Many of the diagrams in this chapter will show a regression line representing a least-squares fit to the precipitation data and error lines reflecting the variability in the data.

Soil-zone Processes that Influence Water Compositions

In arid regions, such as southern Nevada, the average net infiltration rate is generally very low (Flint and Flint 1994). As a result, dust (dry-fall) and solids dissolved in precipitation (wet-fall) accumu-

late in the near-surface environment. Over time, this accumulation process can result in the formation of pedogenic horizons enriched in clays, calcite, silica, gypsum, and, in some cases, highly soluble salts (Watson 1992). The formation of these accumulations or horizons can have major impacts on the chemistry of waters that percolate into the unsaturated zone in these environments.

Recharge water to the unsaturated zone within Yucca Mountain passes through the upper surfaces of the mountain, whereas waters in the saturated zone beneath the mountain appear to represent recharge that infiltrated through soils located at higher elevations within and north of the area of Pahute Mesa that are hydrologically upgradient of Yucca Mountain (Winograd and Thordarson 1975).

The soils on Yucca Mountain and Pahute Mesa are not the same. Soils on Yucca Mountain locally contain abundant caliche and silica horizons (Taylor 1986) and support only limited vegetation. Pahute Mesa soils have little or no caliche and support a greater abundance and variety of vegetation (Spaulding 1985). Soil processes in both of these areas need to be considered in terms of potential impacts on groundwater chemistry. The two soil-zone processes that appear to have the greatest influence on the composition of infiltrating waters are evapotranspiration and dissolution/precipitation of solid phases in the soil.

Evapotranspiration

The term evapotranspiration refers to the loss of water from the soil zone as a result of simple evaporation and transpiration by plants (Freeze and Cherry 1980). Evapotranspiration causes the dissolved-solids content of soil waters to increase. A convenient measure of the amount of evapotranspiration and, by inference, the net infiltration rate associated with a given water sample is its chloride-ion concentration (Scalon 1991). Chloride salts of the major cations have high solubilities, and because Yucca Mountain bedrock is not a significant source of chloride to present-day groundwaters (Fabryka-Martin et al. 1996), the concentration of chloride in these waters can be used to estimate net infiltration rates. The following equation is used to derive this estimate.

$$R = \frac{[\text{Cl}^-]_{\text{precip}}}{[\text{Cl}^-]_{\text{water}}} P, \quad (2)$$

where R is the infiltration rate, $[\text{Cl}^-]_{\text{precip}}$ is the average chloride concentration in precipitation, $[\text{Cl}^-]_{\text{water}}$ is the chloride concentration in the water samples, and P is the rate of precipitation.

According to Hevesi et al. (1992), the average annual precipitation rate at Yucca Mountain is currently 170 mm/yr. If we assume an average chloride concentration in precipitation of 0.55 mg/l (Table 7), the concentration of chloride in water samples from Yucca Mountain can be used to calculate net infiltration rates.

The highest measured chloride concentration (245 mg/l) occurs in one of the shallowest and presumably youngest pore-water samples from the Yucca Mountain Member of Paintbrush Tuff (Fig. 11). The infiltration rate calculated for this sample is 0.4 mm/yr. Pore waters from other Paintbrush Tuff nonwelded units have significantly lower chloride concentrations (30–100 mg/l) and are associated with net infiltration rates of 0.9 to 3 mm/yr. The chloride concentrations in pore-water samples from the Topopah Spring nonwelded units are at the high end of the range observed in the nonwelded vitric units of Paintbrush Tuff. This suggests net infiltration rates were lower when the Topopah Spring pore waters were infiltrated compared to the waters in the overlying Paintbrush Tuff, excluding the Yucca Mountain Member. Presumably, this reflects a drier climate at the time the Topopah Spring pore waters were infiltrated.

The Calico Hills pore-water samples show a range in chloride concentrations from 15 to 82 mg/l. This range overlaps with the Paintbrush Tuff pore-water samples (excluding the Yucca Mountain Member sample) but is lower than the Topopah Spring pore waters. This result could reflect higher net infiltration rates for the Tuff of Calico Hills samples compared to the Topopah Spring samples, or it could simply reflect dilution as discussed further below. Water samples from Prow Pass Member are interesting in that *groundwaters* at the 528-m level have low chloride concentrations whereas *pore waters* from this level are at the high end of the distribution of chloride concentrations found in Tuff of Calico Hills pore waters. This observation indicates that equilibration of saturated-zone groundwaters with pore waters must be a very slow process.

Measured chloride concentrations in perched waters are similar to concentrations observed in saturated-zone groundwaters (Fig. 12). The calculated infiltration rates for these samples range from 2.5 mm/yr for UE-25 p#1 groundwater to 22.8 mm/yr for perched water from SD-7. Clearly, perched waters and saturated-zone groundwaters

reflect much higher infiltration rates than do the unsaturated-zone pore waters. Whether the higher infiltration rates for perched waters reflect a previous wet climate at Yucca Mountain or simply unusually wet years in the modern-day climate cannot be discerned from the water-composition data alone. However, the large difference (factor of 10) in chloride concentrations between pore waters and perched waters in samples from the same depth (for example, UZ-16 at 528 m) support a young age for the perched waters, as diffusion processes would tend to equalize these concentrations over time. It is interesting that similar differences in chloride concentrations between pore waters and fracture waters have been observed at Rainier Mesa (White et al. 1980).

It must be emphasized that the calculated infiltration rates cited in this section are only as good as the assumptions on which they are based. These assumptions include a constancy of the annual precipitation rate, a constancy of chloride concentrations in precipitation, the representativeness of the average chloride concentration in precipitation used in the calculations, and the lack of chloride leaching from rocks in contact with the water. The fact that the calculated infiltration rates are in the same range as those based on field measurements, as reported by Flint and Flint (1994), does lend support to this approach.

Dissolution/precipitation of solid phases in the soil zone

If concentration (that is, enrichment) of dissolved

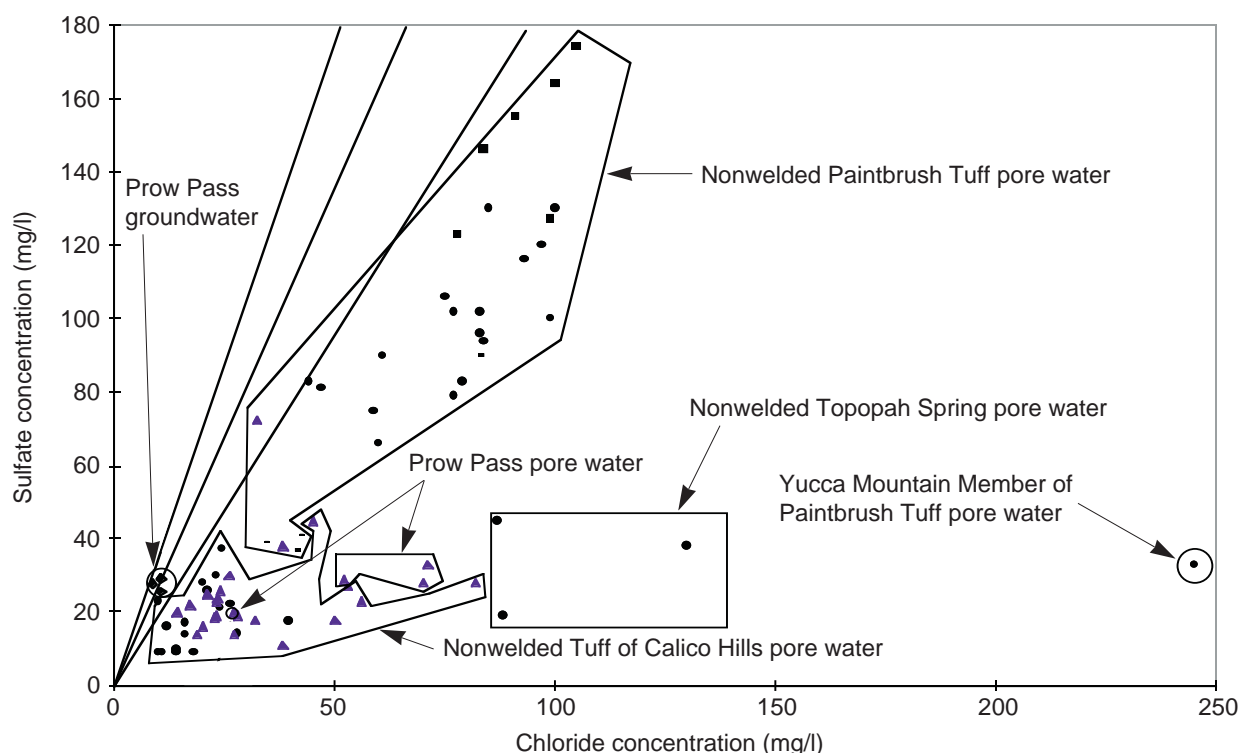


Figure 11. Sulfate versus Chloride in Pore Water. This plot shows sulfate versus chloride concentrations for unsaturated-zone pore-water samples and for three saturated-zone groundwater samples from Prow Pass (all data from Yang et al. 1988, 1996). The central line represents the best-fit line through composition data for precipitation at the Kawich Range sites (see Fig. 10), and the two outer lines reflect one-sigma variability in those precipitation compositions. (Drill-hole designations for the unsaturated-zone data points: circles: UZ-14; triangles: UZ-16; squares: UZ-4; and horizontal bars: UZ-5.)

constituents by evapotranspiration were the only soil-zone process to impact the composition of infiltrating waters, the concentrations of other major constituents in these waters could be obtained from the net infiltration rate (that is, the chloride concentration) and the ratio of the concentration of the constituent of interest relative to the concentration of chloride in precipitation. However, the presence of soil horizons on Yucca Mountain that are enriched in calcite, silica, and other components (Taylor 1986) suggests the situation is more complicated. These soil horizons indicate that pedogenic processes involving precipitation and dissolution of these phases have occurred in the soils over time. An important question is: “To what extent did these precipitation/dissolution processes influence the unsaturated-zone water compositions analyzed by Yang et al. (1988, 1996), and to what extent are they likely to influence unsaturated-zone water

compositions in the future?”

Because age dates obtained for the calcite-rich and silica-rich soil horizons tend to be much older (Paces et al. 1995) than those obtained for pore waters, perched waters, and groundwaters at Yucca Mountain (Yang et al. 1996; Waddell et al. 1984), the relationship between the compositions of these horizons and the compositions of various waters presently in Yucca Mountain is uncertain. To establish a connection, evidence for chemical reactions that are unique to the soil zone must be identified in the unsaturated-zone water compositions.

Sulfate and chloride ions are generally conservative constituents in dilute oxidizing waters such as the unsaturated-zone pore waters in Yucca Mountain. Therefore, we would expect a plot of sulfate and chloride concentrations to show sulfate

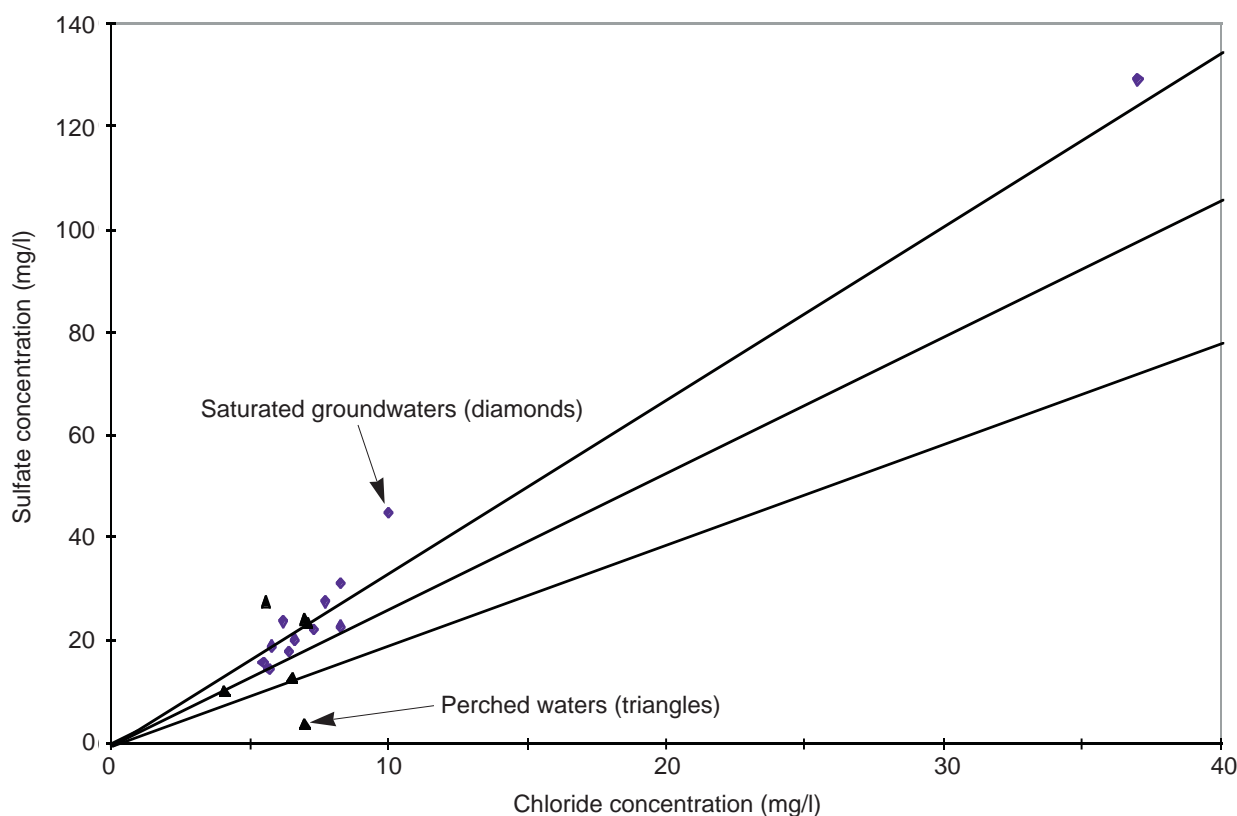


Figure 12. Sulfate versus Chloride in Perched Waters and Groundwaters. This plot shows sulfate versus chloride concentrations for perched waters and saturated-zone groundwaters. The lines are the same precipitation and variation lines as those plotted in Fig. 11.

to chloride ratios similar to those observed in precipitation. However, as shown in Fig. 11, unsaturated-zone pore waters analyzed by Yang et al. (1988, 1996) show sulfate-to-chloride ratios consistently lower than the ratios observed in recent precipitation. Because all the unsaturated-zone pore-water analyses are grossly undersaturated with chloride phases and with gypsum and other possible sulfate phases involving the major cations, it is unlikely that solid chloride or sulfate phases are precipitated in the unsaturated zone.

Drever and Smith (1978) presented a model that offers one potential explanation for the low sulfate-to-chloride ratios in the unsaturated-zone pore waters. Their model involves drying and wetting cycles in the soil zone. During the drying phase, the concentrations of dissolved solutes are increased in the soil waters by evapotranspiration to the degree that phases such as calcite, gypsum, silica, and the more soluble salts precipitate. During “occasional heavy rains,” the phases precipitated during the drying phase are partially redissolved. Because the dissolution rates for highly soluble salts, such as sodium chloride, are higher than the rates for less soluble salts, such as calcite, gypsum, and silica, a portion of the less soluble salts may remain undissolved after the “occasional heavy rains” infiltrate through the soil zone. In terms of sulfate and chloride concentrations, this process could lead to soil waters with lower sulfate-to-chloride ratios than those observed in precipitation. The actual concentrations of sulfate and chloride in these waters would depend on the details of the processes involved, including the dissolution kinetics of the sulfate and chloride phases, the residence time of the waters in the soil zone, and the original masses of sulfate and chloride in the soil zone.

Although differences in the dissolution kinetics of sulfate and chloride salts may be part of the explanation for the low sulfate-to-chloride ratios in pore waters from the unsaturated zone at Yucca Mountain, these differences are likely augmented, and perhaps even dominated, by crystallization-

sequence effects. For example, it is possible that minerals, such as calcite and gypsum, that precipitate from evaporating pore waters early in a crystallization sequence are partially or completely sequestered by minerals that precipitate later in the sequence (such as being coated by opal-A and halite). Alternatively, early-crystallized phases may completely fill smaller pores in the rocks and, therefore, be less accessible to infiltrating waters than minerals crystallized later in the sequence in larger pores (for example, Chadwick et al. 1987). During subsequent infiltration events, the latest-formed phases in pores accessible to infiltrating waters would preferentially dissolve, leading to soil solutions enriched in the more soluble salts relative to the less soluble salts.

When viewed from the perspective of this model, chloride and sulfate concentrations for the pore-water sample from the Yucca Mountain Member tuff (Fig. 11) suggest this sample reflects an infiltration event that followed an extended “dry” period of lower than average precipitation. In fact, the chloride concentration of this sample would represent approximately 450 liters of precipitation (rain and snow), assuming an average chloride concentration of 0.55 mg/l for precipitation (Table 7). During the “dry” period, the sulfate concentration in the soil water must have increased to the point where sulfate minerals such as gypsum crystallized from the soil solution. Chloride minerals may also have crystallized at this time. For some extended period, net infiltration into the soil zone was insufficient to wash these pedogenic minerals out of the zone. During this time, these minerals may have been repeatedly dissolved and recrystallized. Eventually, a large precipitation event caused sufficient water to infiltrate the soil zone so that water percolated out of that zone into the unsaturated zone, carrying most of the accumulated chloride and lesser amounts of the accumulated sulfate.

We can estimate the amounts of gypsum and calcite precipitated from the Yucca Mountain Member sample by 1) assuming that soil-zone waters originally had the composition of recent precipitation,

2) assuming that sufficient soil water evaporated so that the chloride concentration in the remaining liquid equals that measured in the Yucca Mountain Member sample, 3) calculating the amount of precipitated gypsum as the difference in the measured sulfate concentration and that inferred from the evaporated precipitation, 4) subtracting enough calcium from the evaporated precipitation to produce the gypsum, 5) assuming that enough calcite precipitated with the remaining calcium so that the concentration measured in the sample is the remainder, and 6) assuming that chloride minerals were totally dissolved by the large infiltration event. The resulting calculated amounts are approximately 700 mg of gypsum and 200 mg of calcite per liter of the Yucca Mountain Member sample.

Pore waters from Paintbrush Tuff, Topopah Spring, Prow Pass, and Tuff of Calico Hills have lower chloride concentrations and lower sulfate-to-chloride ratios than the Yucca Mountain Member sample. According to the model, these would reflect infiltration events that followed shorter “dry” periods. However, there is an additional complication in the sulfate and chloride data for these waters—there is a range of sulfate-to-chloride ratios at a given chloride concentration. If the precipitation of sulfate in the soil zone is the explanation for the deviation of these compositions from evapotranspired precipitation, it is disconcerting that this process appears to produce such a large range of sulfate-to-chloride ratios.

One possible explanation is that the range simply reflects the variability in the infiltration process. For example, if the pore sizes in the sulfate-mineral accumulation horizon are much smaller in one location than another, infiltrating waters may be denied access to a large fraction of the pores in the former case as a result of plugging by early-formed phases (Taylor 1986; Levy 1984). Alternatively, a mixing process could be involved. The rather narrow range of sulfate concentrations (10–40 mg/l) observed for the Calico Hills, Topopah Spring, and Prow Pass samples and the fact that this range

includes most perched and saturated-zone samples is suggestive of such a process. The mixing could involve perched or saturated-zone waters with low sulfate and chloride concentrations and pore waters with low sulfate and high chloride concentrations, such as the Yucca Mountain Member sample. Unfortunately, the lack of certainty in the explanation for the variations in sulfate-to-chloride ratios precludes the development of a quantitative model for this process. More information on the detailed hydrology of Yucca Mountain soils is required.

The conceptual model and the calculations described above imply that sulfate minerals will accumulate in the soil zone on Yucca Mountain. However, analyses of Yucca Mountain soils only occasionally show significant amounts of gypsum, although small amounts (1–2%) are routinely detected (Taylor 1986; Vaniman et al. 1995). The fact that gypsum is not more common in Yucca Mountain soils could be due to a variety of factors including 1) sulfate minerals were not accumulated in soil profiles prior to the last few thousand years as the climate became drier (Spaulding 1985), 2) sulfate minerals occur deeper in the soil profile than the depths covered by the analyses, 3) sulfate minerals were more abundant in soil profiles previously but were leached out during extended wet periods, or 4) some other process such as microbial reduction of sulfate is causing the decrease in sulfate concentrations.

The last factor is unlikely given the oxidizing nature of the unsaturated-zone pore waters. The third factor is a possibility but is difficult to evaluate with existing data. If this factor was responsible, unsaturated-zone waters would have had sulfate-to-chloride ratios in excess of precipitation for some period of time. There is no clear evidence for this process in analyses of the unsaturated zone (Fig. 11), although it is possible that waters of this type were present in the system but were flushed through to the saturated zone. Factor two is unlikely because significant amounts of gypsum were, in fact, found in some of the profiles described by Taylor (1986). The interpretation

avored in this report is that sulfate minerals were more abundant in soil profiles in earlier times but were subsequently leached out, and the amounts found in soils at the present time only reflect the most recent (“dry”) climatic regime.

Another important constituent in soil waters is silica. Silica is important because it is by far the most abundant constituent in the volcanic rocks of Yucca Mountain and its concentration in solution has a major impact on the ability of the solution to dissolve additional mineral components. Silica-rich horizons are often interbedded with calcite-rich horizons on Yucca Mountain (Taylor 1986). A model for the origin of silica-rich horizons in soils derived from volcanic rocks was developed by Chadwick et al. (1987). This model involves the reversible adsorption of silica onto surfaces of other soil constituents (for example, clays, sesquioxides, and weathered primary minerals) and the formation of opaline silica sols and coatings as soils dry out. Silica in these types of soils is apparently quite easily solubilized. Chadwick et al. (1987) found that up to 152 mg/l of monomeric silica could be extracted from the soils in 16 hours. These results are consistent with other reports (for example, Gifford and Frugoli 1964) and suggest that waters percolating from the soil zone into the unsaturated zone at Yucca Mountain will be close to saturation with amorphous silica.

The soil zone is also important to carbon-dioxide partial pressures in the unsaturated zone. The partial pressure of CO₂ in soil atmospheres is commonly elevated over the partial pressure of CO₂ in the earth’s atmosphere (Greenland and Hayes 1978). Measurements of the partial pressure of CO₂ at a depth of 10 feet in the unsaturated-zone drill hole UZ-1 in Yucca Mountain indicate that it is approximately four times the atmospheric value (Yang et al. 1996). This fact suggests that soil-zone processes at the surface of Yucca Mountain could influence the partial pressure of CO₂ in the unsaturated zone. However, the fact that CO₂ partial pressures are quite variable with depth in drill hole UZ-1 suggests there may be additional

sources of CO₂ in the unsaturated zone. Interestingly, the isotopic composition of CO₂ in various wells on Yucca Mountain suggests it has been strongly influenced by biologic activity (Thorstenson et al. 1989; Yang et al. 1996).

Pore-water Compositions above the Potential Repository Horizon

The types of chemical reactions that could affect unsaturated-zone water compositions include 1) dissolution/precipitation reactions, 2) ion-exchange reactions, and 3) gas-phase reactions (Meijer 1995). Because the absolute abundance of ion-exchanging minerals is generally low in units above the zeolitized Tuff of Calico Hills (Bish and Chipera 1989), dissolution/precipitation reactions and gas-phase reactions are likely dominant in this zone and will, therefore, be the focus of this section.

Sulfate-to-chloride ratios in waters from the unsaturated zone suggest there are at least two types of waters in the unsaturated zone above Tuff of Calico Hills (Figs. 11 and 12). These are relatively dilute perched waters and higher-ionic-strength pore waters. Because perched-water compositions are very similar to saturated-zone water compositions (Fig. 12), they will be discussed in the next section (“Perched-water compositions below the potential repository horizon”).

As discussed in Meijer (1995), dissolution reactions in devitrified and vitric silicic tuffs will involve the hydrolysis of feldspar and glass, respectively. These hydrolysis reactions generally leach sodium (\pm calcium, magnesium, and potassium) in exchange for hydrogen ions (White et al. 1980). Therefore, relative to a conservative solute such as chloride, sodium concentrations should increase in the pore waters relative to the original precipitation compositions if hydrolysis reactions are of importance. As shown in Fig. 13, this is contrary to what is observed. In the pore waters from units above Calico Hills (that is, Yucca Mountain Member, nonwelded Paintbrush Tuff, and nonwelded Topopah Spring), sodium-to-chlo-

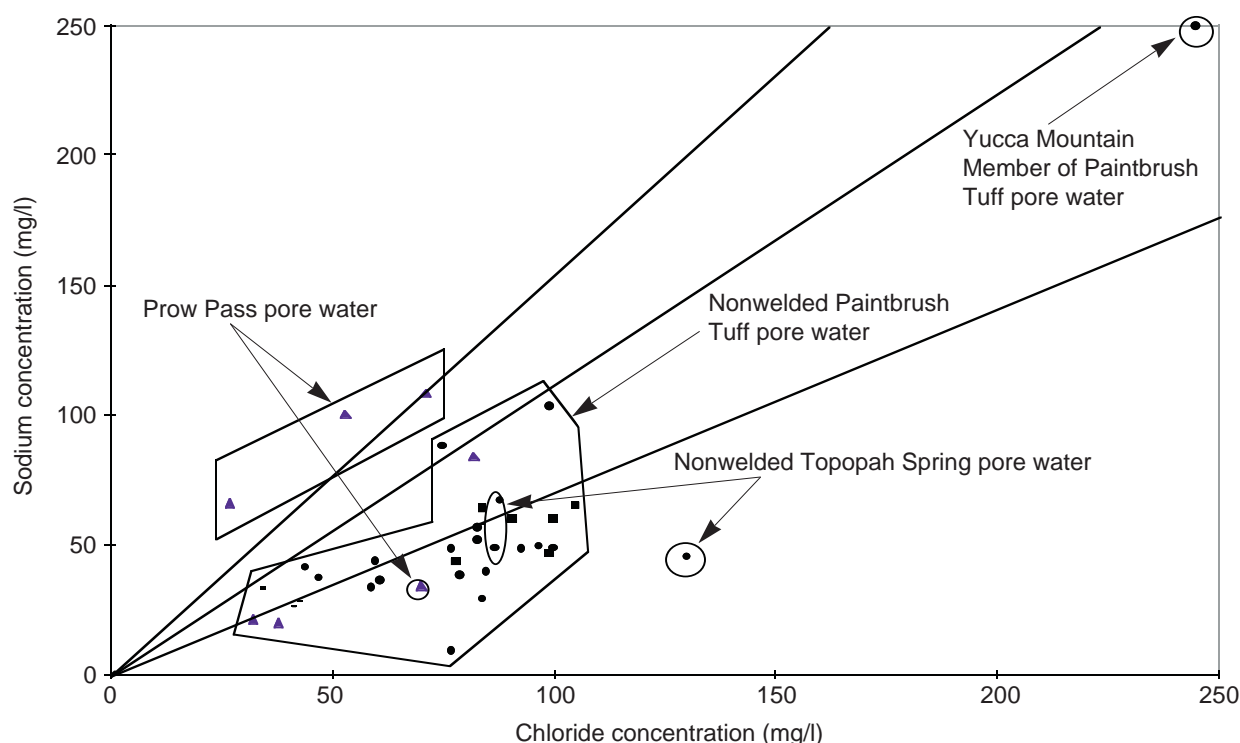


Figure 13. Sodium versus Chloride. This plot shows the sodium (rather than sulfate) concentration versus the chloride concentration of unsaturated-zone pore-water samples from Yucca Mountain. Here, the central line represents a regression fit of sodium-versus-chloride precipitation data, and the outer lines represent one standard deviation for the scatter of those data. (Drill-hole designations for data points: circles: UZ-14; triangles: UZ-16; squares: UZ-4; and horizontal bars: UZ-5.)

ride ratios are generally lower than those observed in modern-day precipitation. This observation implies that hydrolysis reactions have not significantly impacted the chemistry of these waters.

Why sodium-to-chloride ratios in these pore waters are lower than those observed in recent precipitation is not entirely clear. Potential explanations include the possibility that nonchloride sodium salts (for example, sodium sulfate) crystallized in the soil zone prior to chloride-salt crystallization and were sequestered, that precipitation (wet-fall plus dry-fall) had lower sodium-to-chloride ratios in the past, or that ion-exchange reactions (for example, with clays) removed sodium ions from solution. The latter explanation appears unlikely given that clay analyses from units at this level are enriched in calcium and magnesium, not sodium

(Levy 1984). Resolution of this question will require additional investigations of the soil-zone processes at Yucca Mountain.

The lack of evidence in the sodium-versus-chloride concentration data for hydrolysis reactions in units above Calico Hills is not unexpected and is, in fact, corroborated by other observations. These observations include the persistence of abundant 10-to-12-million-year-old volcanic glass in the unsaturated zone within Yucca Mountain and the fact that, with some exceptions, only limited amounts of secondary minerals are found in the glassy and devitrified tuffs (Bish and Chipera 1989). The exceptions are the localized clay-rich horizons in parts of the nonwelded Paintbrush Tuff. The origin of these horizons is uncertain at the present time. They may reflect alteration of glass in high-flow

(water) zones (Levy 1984), or they may have formed during weathering reactions that occurred while the tuffs were exposed at the surface.

The lack of evidence for hydrolysis reactions in the sodium-versus-chloride concentration data for pore waters in units above Calico Hills likely reflects the fact that concentration of cations (for example, sodium) by evapotranspiration combined with the saturation of infiltrating waters with amorphous silica in the soil zone has lowered the reactivity of these waters with respect to dissolution of the aluminosilicate solids (such as feldspar and glass). For feldspars, this can be quantified by calculating the saturation state of the pore waters with respect to feldspar minerals. Aluminum and potassium concentrations were not reported for pore waters by Yang et al. (1988, 1996), precluding direct calculation of feldspar saturation states. However, the high sodium and silica concentrations in the pore waters ensure that they will be saturated with albite when in contact with a solid source of aluminum (such as feldspar or glass). This effect implies that the feldspars in the devitrified tuffs will not be significantly altered by the waters percolating out of the soil zone. The observed lack of secondary minerals in the devitrified zones (Bish and Chipera 1989) corroborates this conclusion.

In the case of volcanic glass, the situation is less straightforward because glass is thermodynamically unstable with respect to secondary minerals at ambient temperatures and pressures. In fact, many studies have been carried out in recent years to gain an understanding of glass alteration behavior, mainly to provide a basis for predictions of the alteration behavior of nuclear waste glasses. An important result of these studies is that the glass dissolution rate has been shown to be quite sensitive to the silica concentration in solution. As this concentration reaches saturation with amorphous silica, the dissolution reaction slows down dramatically (Grambow 1992). Apparently, for glass alteration to proceed, the “gel reaction zone” that forms on the glass surface needs to dissolve. If the solution phase is saturated with amorphous silica, the

dissolution of this material is inhibited because the affinity of the dissolution reaction is low.

Conceivably, other silica polymorphs with lower solubilities (for example, opal C-T, cristobalite, and quartz) could nucleate and crystallize, thereby causing the silica concentration in solution to be maintained at a lower level. This effect, in turn, could enhance the glass dissolution rate. However, the nucleation rates of these other polymorphs appear to be inhibited for some reason that remains to be determined.

The concentrations of silica in unsaturated-zone pore waters are generally high (Fig. 14). Although essentially all of the pore-water samples analyzed by Yang et al. (1988, 1996) are saturated with α -cristobalite, many are saturated with opal-CT and some are even saturated with opal-A at 25°C (Fig. 14). The concentrations tend to be higher in pore-water samples from Paintbrush Tuff and Tuffs of Calico Hills compared to samples from Topopah Spring and Prow Pass. Temperature does not appear to be a controlling parameter. Also, there do not appear to be consistent trends in silica concentration with depth in a given unit. The high silica concentrations in the Paintbrush Tuff pore waters presumably reflect the presence of abundant glass in this unit. The slightly lower silica concentrations in Tuff of Calico Hills pore waters may reflect the fact that the mineralogy of the host rock consists of zeolites and opal-CT (Bish et al. 1996b). The mineralogy of the Topopah Spring and Prow Pass tuff samples in drill holes UZ-14 and UZ-16 was not available at the time this report was being written.

Part of the scatter in the silica data plotted in Fig. 14 may reflect analytical techniques. The pore-water samples were not filtered prior to analysis, and the analyses were carried out by inductively coupled plasma-emission spectroscopy, which does not discriminate monomeric silica from other forms of silica in solution. This is likely the explanation for the high silica concentrations (> 80 mg/l) measured in some of the Calico Hills pore-water samples. The analyses of these samples also

showed some relatively high alumina concentrations, which are an indication of the presence of particulate matter (for example, colloids), as aluminum is very insoluble in near-neutral solutions. At this point, it is difficult to quantify the controls on pore-water silica concentrations at ambient temperatures other than to say that as long as volcanic glass remains in the unsaturated zone, these concentrations will be in a range between saturation with α -cristobalite and saturation with opal-A.

The concentration of bicarbonate in Yucca Mountain waters is an important parameter with respect to the solubility and sorption of many of the radionuclides in high-level radioactive waste (GCX 1994). The data presented by Yang et al. (1996) show that pore waters in the units above Tuff of Calico Hills tend to have bicarbonate-to-

chloride ratios that are equal to or below the average observed in recent precipitation (Fig. 15). This trend likely reflects the crystallization of calcite in the soil zone prior to percolation of the waters into the unsaturated zone. If hydrolysis reactions were important in the evolution of these waters, bicarbonate-to-chloride ratios would exceed those observed in precipitation. This result is, in fact, observed in the analyses of perched waters, saturated-zone groundwaters, and pore waters from Tuff of Calico Hills, as discussed in more detail in the next section on perched-water compositions.

Calcite dissolution and precipitation is also likely to exert a major influence on the calcium concentration in pore waters in units above the zeolitized tuff in Calico Hills. Unfortunately, quantitative modeling of calcite dissolution/precipitation

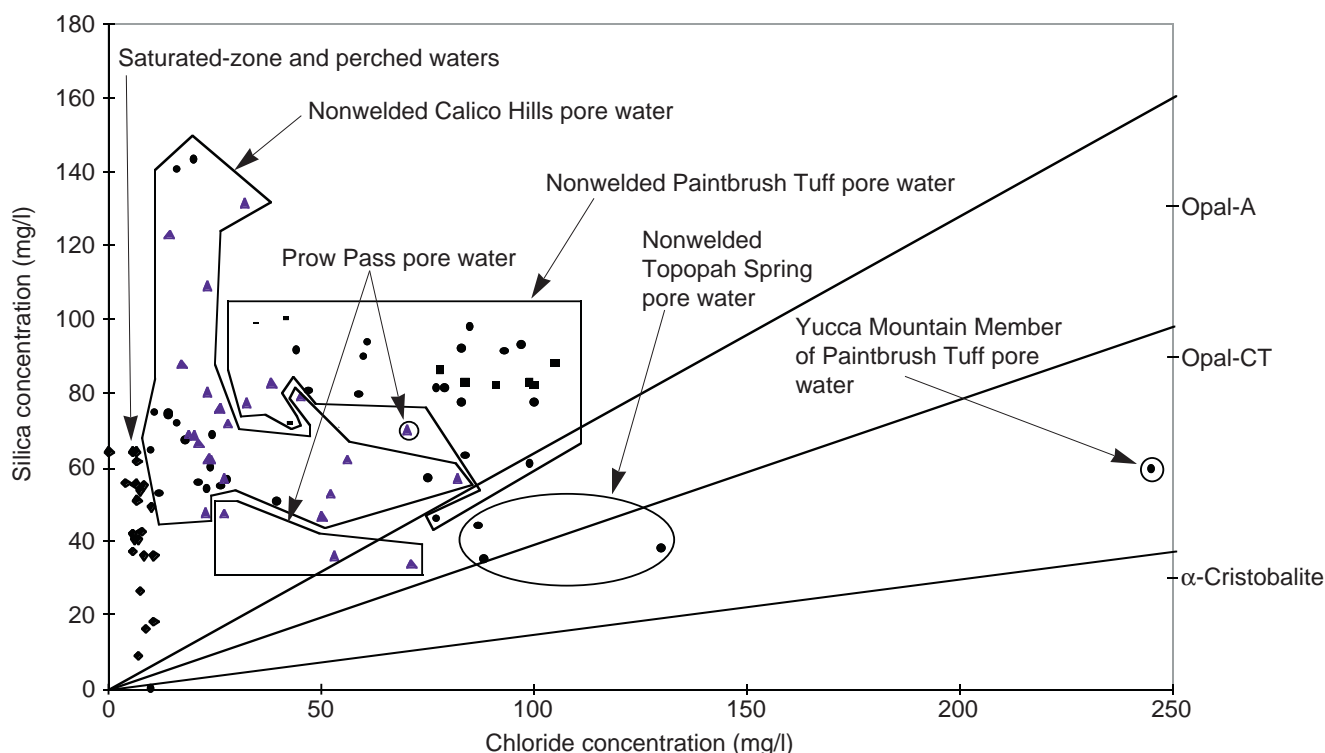


Figure 14. Silica versus Chloride. This plot shows silica versus chloride concentrations in pore waters, perched waters, and saturated-zone groundwaters (perched and saturated-zone data are not differentiated). The silica concentrations at which the waters would be saturated with opal-A, opal-CT and α -cristobalite at 25°C are given on the right. The straight lines are the regression fit to silica-versus-chloride concentrations in precipitation and the one-sigma deviations. (Drill-hole designations: circles: UZ-14; triangles: UZ-16; squares: UZ-4; horizontal bars: UZ-5; and diamonds: perched and saturated-zone waters.)

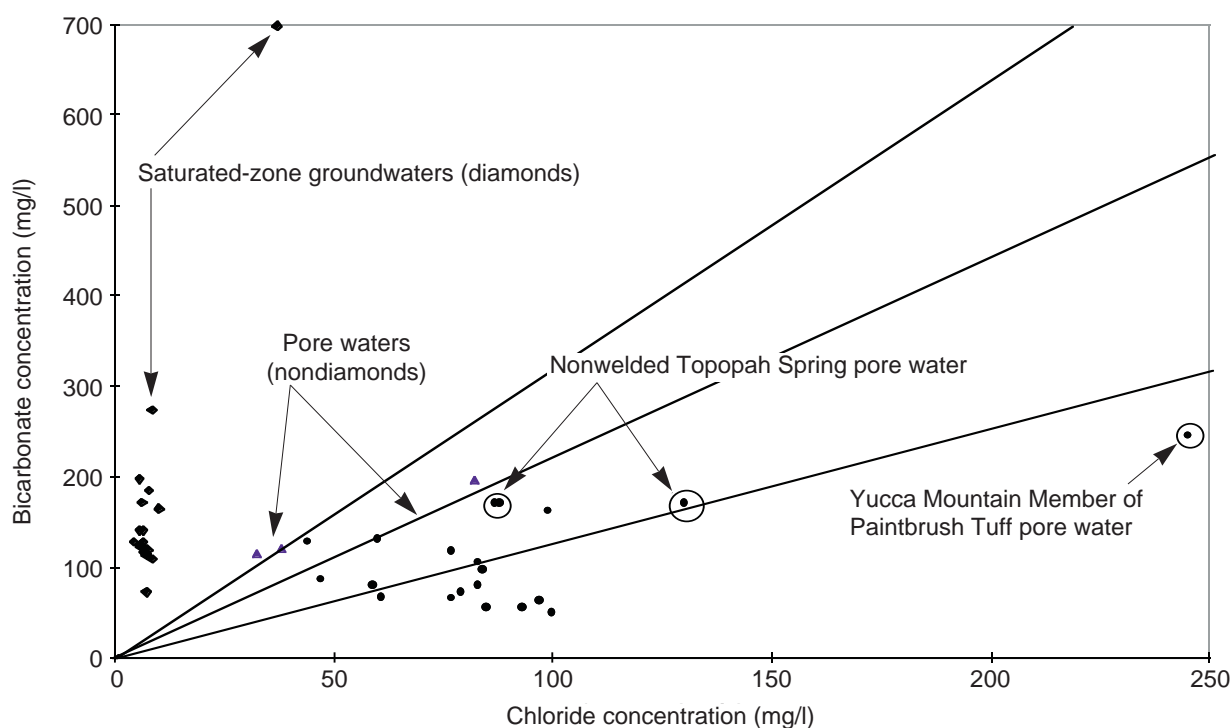


Figure 15. Bicarbonate versus Chloride. This plot shows bicarbonate versus chloride concentrations in pore waters from units above Tuff of Calico Hills and in saturated-zone groundwaters. The central line shows bicarbonate versus chloride concentrations in precipitation; the outer lines are the one-sigma deviations. (Drill-hole designations: circles: UZ-14; triangles: UZ-16; diamonds: saturated-zone waters.)

behavior in the unsaturated zone at Yucca Mountain is complicated by the fact that the partial pressure of carbon dioxide in the gas phase present in the unsaturated zone appears to be quite variable (Yang et al. 1996). Detailed gas-composition data have been collected from borehole UZ-1 for over ten years. These data show that, for some as yet undetermined reason, that the partial pressure of carbon dioxide in the unsaturated zone exceeds the atmospheric value (0.00032 atmospheres) at nearly all depths sampled. The pressure is approximately 0.01 atmospheres in the alluvium and decreases to approximately 0.0003 atmospheres in the middle tuff of Topopah Spring. Below this depth, it increases to values in excess of 0.003 atmospheres in the lower portion of Topopah Spring where the borehole bottoms out. Data for the partial pressure of carbon dioxide in the gas phase in units below the lower tuff of Topopah Spring are not available.

By combining pore-water compositions from borehole UZ-14 with carbon-dioxide partial pressures reported for borehole UZ-1 (Yang et al. 1996), located in close proximity to UZ-14, the saturation state of calcite in the pore waters can be calculated (Table 8). The values of the calcite saturation index presented in that table reflect the degree to which the water is saturated with calcite. Positive numbers reflect oversaturation and negative numbers reflect undersaturation. It is of interest that only the sample from the Yucca Mountain Member (UZ14-45, which is from borehole UZ-14 at 45 feet) shows a positive value. The sample at 135 feet is close to saturation, whereas the other samples are undersaturated and, therefore, could dissolve calcite if it were present. Because data on the partial pressure of carbon dioxide are not available for pore-water samples from other boreholes, calcite saturation cannot be realistically evaluated for these.

Table 8. Calculated Calcite Saturation Indices

Sample ID	Saturation Index*
UZ14-45	0.0153
UZ14-85	-0.1835
UZ14-91	-0.2485
UZ14-95	-0.5756
UZ14-96	-0.5503
UZ14-100	-0.6820
UZ14-114	-0.7885
UZ14-135	-0.0158
UZ14-144	-0.2219
UZ14-147	-0.6269
UZ14-177	-0.8767
UZ14-178	-0.1829
UZ14-215	-0.8890
UZ14-225	-0.7191
UZ14-235	-0.4746
UZ14-240	-0.4952
UZ14-245	-0.7692
UZ14-1258	-0.0389

* $\log(IAP/K_T)$, where $IAP = [Ca^{2+}][CO_3^{2-}]$ is the measured ion association product for the water and K_T is the equilibrium product for the solubility of calcite at the temperature of interest.

The fact that most of the UZ-14 pore-water samples are undersaturated with calcite is not surprising given the spotty distribution of calcite in Yucca Mountain (Vaniman and Chipera 1996). Calcite is more likely to be precipitated in fractures for which the partial pressure of carbon dioxide is lower as a result of more direct access to the atmosphere. Because the total amount of calcite in fractures is small relative to the total mass of solute in pore waters, precipitation/dissolution reactions involving fracture calcite are unlikely to control pore-water calcium concentrations.

The elevated partial pressure of carbon dioxide will tend to keep the pH in the pore waters in the range from 7 to 8. If carbon-dioxide partial pressures in the unsaturated-zone gas phase decrease with time due to venting associated with operations at the potential repository, the pH of pore waters could

increase to values above 8, depending on the extent of degassing. Because the total volume of the excavations are small relative to the total volume of the rock mass surrounding the potential repository, it is unlikely this effect will be very significant overall.

The concentrations of the major cations in pore waters are of interest with respect to the solubility and sorption behavior of the radionuclides in high-level radioactive waste. As noted above, the generally low abundances of ion-exchanging minerals in the units above the zeolitized Tuff of Calico Hills suggest that cation proportions in pore waters from this portion of Yucca Mountain will reflect primarily soil-zone precipitation/dissolution processes. As shown in Fig. 16, the calcium-to-chloride ratios in pore waters from units above Tuff of Calico Hills are either on the precipitation line or below it. Sodium-to-chloride ratios in these samples also plot below the precipitation line (Fig. 13). If ion-exchange reactions were controlling the relative concentrations of calcium and sodium, there would be an antithetic relationship in their concentrations. This relationship is not evident in the data, which suggests that ion-exchange reactions are of secondary importance relative to other reactions that involve these elements, such as the precipitation of calcite, gypsum, and other salts in the soil zone.

The oxidation-reduction potential (Eh) of waters in the unsaturated zone should reflect the fact that the gas phase in the unsaturated zone has an oxygen partial pressure equal to that in the atmosphere (Thorstenson et al. 1989; Yang et al. 1996). This condition will cause the Eh to be in the range from 400 to 600 mV.

The pH of pore waters in the unsaturated zone will reflect the partial pressure of carbon dioxide in the gas phase. Because this partial pressure is variable with depth (Yang et al. 1996) and above atmospheric levels, the pH of the pore waters will vary in a range from approximately 7 to 8.

Bounds on future variations in the composition of

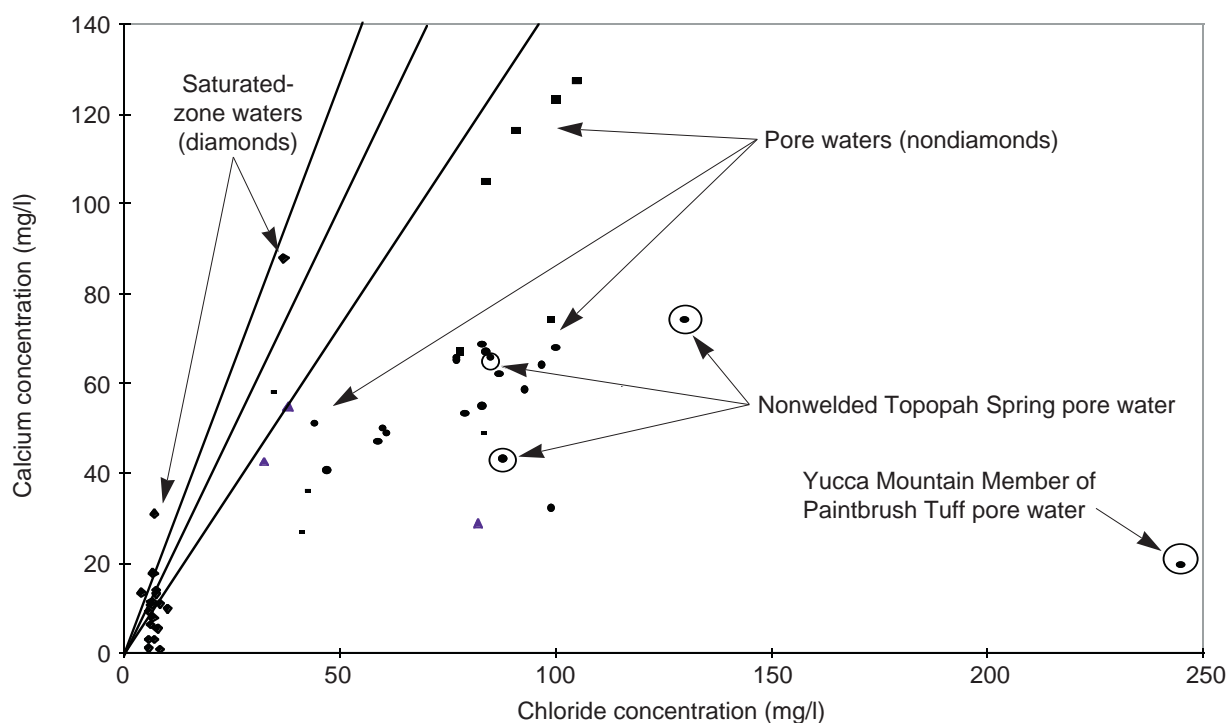


Figure 16. Calcium versus Chloride. This plot shows calcium versus chloride concentrations of unsaturated-zone pore waters from units above Tuff of Calico Hills and of saturated-zone groundwaters. The straight lines are the regression fit of precipitation data for calcium versus chloride and the one-sigma deviations from that fit. (Drill-hole designations: circles: UZ-14; triangles: UZ-16; squares: UZ-4; horizontal bars: UZ-5; diamonds: saturated-zone waters.)

pore waters in units above and within the repository horizon are difficult to determine solely on the basis of chemical arguments. The main controls on these compositions are the amount of evapotranspiration that occurs in the soil zone and precipitation reactions in the soil zone. High amounts of evapotranspiration will lead to pore waters with high ionic strength. Such waters will tend to precipitate calcite, gypsum, silica, and possible other soluble salts. Fortunately, the higher the evapotranspiration, the less infiltration there will be. In other words, high-ionic-strength pore waters will be of limited volume and may not percolate to the level of the potential repository over its useful lifetime. Because the detailed soil hydrology can have a significant impact on the chemical evolution of soil waters, a coupled flow-chemistry model is required to properly model the evolution of these waters.

Perched-water Compositions below the Potential Repository Horizon

Sulfate-to-chloride ratios in perched and saturated-zone waters show little evidence of soil-zone precipitation reactions involving gypsum and other soluble sulfate salts. In fact, they show sulfate-to-chloride ratios that are somewhat higher than those observed in precipitation (Fig. 12). This result may reflect somewhat higher sulfate-to-chloride ratios in the precipitation when these waters were infiltrated, or the waters may be dissolving small amounts of sulfate as they infiltrate through the soil zone and the unsaturated zone.

An important characteristic of perched waters, saturated-zone groundwaters, *and* many of the pore waters in Tuff of Calico Hills is that these waters all have elevated bicarbonate-to-chloride and sodi-

um-to-chloride ratios relative to the ratios observed in recent precipitation (Figs. 17 and 18). This observation suggests that these waters have been subject to hydrolysis reactions (White et al. 1980). In these reactions, hydrogen ions resulting from the dissociation of carbonic acid exchange with cations in the solid phase. An example of such a reaction involving sodium is



Elevated bicarbonate-to-chloride ratios provide the most definitive evidence of hydrolysis reactions because elevated sodium-to-chloride ratios could also reflect ion-exchange processes.

The fact that pore waters in the Topopah Spring Member overlying Tuff of Calico Hills do not show evidence of significant hydrolysis reactions suggests that either hydrolysis reactions are currently operative in Tuff of Calico Hills or that the Calico Hills pore waters contain water from another source. Pore waters from Prow Pass Member, which underlies Tuff of Calico Hills, have bicarbonate-to-chloride ratios similar to those observed in tuff from Topopah Spring Member. Therefore, the high bicarbonate-to-chloride ratios in pore waters from Calico Hills are sandwiched between units with low bicarbonate-to-chloride pore waters. Interestingly, *groundwater* pumped from Prow Pass Member in borehole UZ-16 has bicarbonate-to-chloride ratios that are much higher than those observed in recent precipitation and that are similar to those observed in the pore waters of Calico Hills. This fact suggests that the higher bicarbonate-to-chloride ratios in the pore waters of Calico Hills are not simply the result of in-situ hydrolysis reactions. If they were, similar bicarbonate-to-chloride ratios would be observed in Prow Pass pore waters. The important point is that pore waters in Tuff of Calico Hills and groundwaters from below the water table have compositions that are distinct from the compositions of pore waters in the units above and below Tuff of Calico Hills.

The relative importance of hydrolysis and ion-

exchange reactions in these waters can be approximated as follows. Assume that the “excess” bicarbonate (the amount in excess of that indicated by the precipitation ratio at the given chloride concentration) in these waters reflects only hydrolysis reactions and also that the amount of sodium released to solution during the reaction is approximately 0.6 equivalents of sodium per equivalent of bicarbonate (White et al. 1980). The amount of sodium in the water analysis in excess of that originally in the water (from the sodium-to-chloride ratio in precipitation) plus the sodium released through hydrolysis reactions is assumed to be the amount contributed to the solution by ion-exchange reactions. This calculation suggests that up to 95% of the “excess” sodium in solution (relative to precipitation) appears to be contributed by hydrolysis reactions. The relatively small proportions that appear to be contributed by ion-exchange reactions in pore waters from Tuff of Calico Hills are more or less consistent with the amounts of calcium and magnesium lost from these waters (relative to precipitation) (Figs. 19 and 20).

The Calico Hills pore waters are interesting in that in addition to showing evidence of hydrolysis reactions in their bicarbonate-to-chloride and sodium-to-chloride ratios (Figs. 17 and 18), they also show evidence of soil-zone processes in their sulfate-to-chloride ratios (Fig. 11). That is, these latter ratios are well below those observed in recent precipitation. As discussed above, the sulfate-to-chloride ratios in these pore waters could reflect mixing of perched or saturated-zone waters with pore waters percolating into Tuff of Calico Hills from Topopah Spring Member. If this is true, the high bicarbonate-to-chloride ratios in these pore waters would also be a result of the mixing of these waters. The proportions of perched/saturated-zone water and Topopah Spring pore water in the hypothetical mixtures can be estimated on the basis of chloride concentration of the Topopah Spring samples and the perched/saturated-zone samples at a given bicarbonate concentration. These estimates fall in the range of from 60 to 90% perched/saturated-zone water and from 10 to 40% pore water.

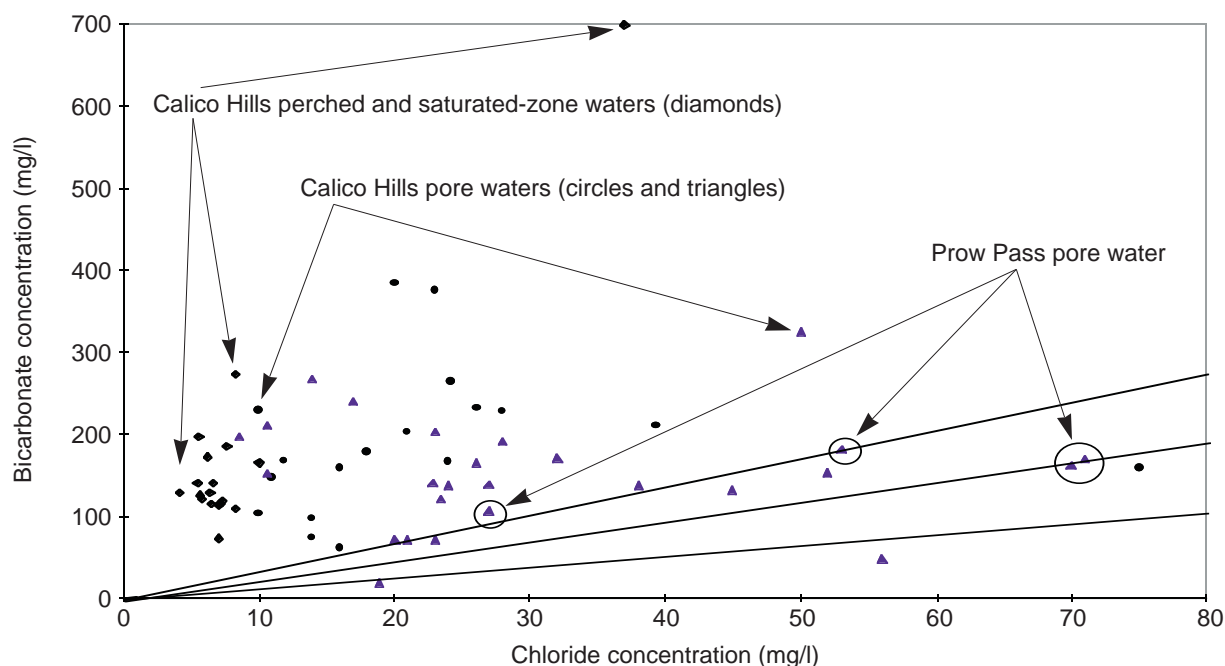


Figure 17. Calico Hills Bicarbonate. This plot shows bicarbonate versus chloride concentrations in Calico Hills pore waters, perched waters, and saturated-zone groundwaters. The straight lines are the regression fit of precipitation data for bicarbonate versus chloride and the one-sigma deviations from that fit. (Drill-hole designations: circles: UZ-14; triangles: UZ-16; diamonds: saturated-zone waters.)

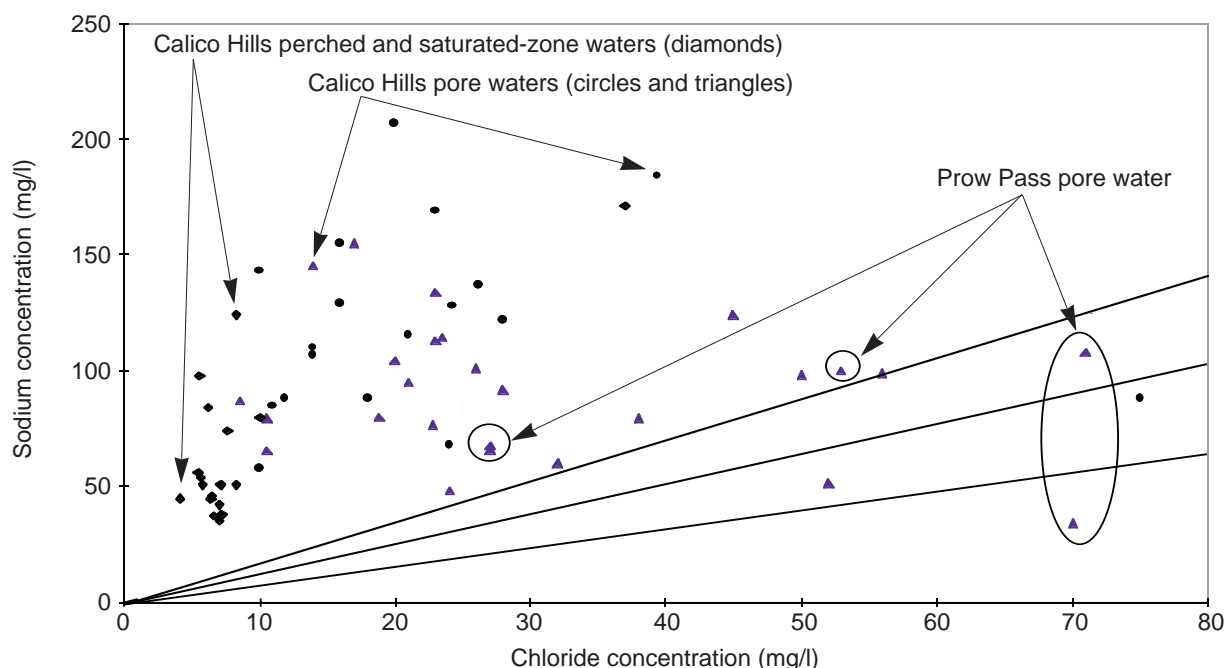


Figure 18. Calico Hills Sodium. This plot shows sodium versus chloride concentrations in Tuff of Calico Hills pore waters, perched waters, and saturated-zone groundwaters. The straight lines are the regression fit and one-sigma deviations for sodium-versus-chloride precipitation data. (Drill-hole designations: circles: UZ-14; triangles: UZ-16; diamonds: saturated-zone waters.)

Whether or not these estimates are representative of waters in Tuff of Calico Hills in other parts of Yucca Mountain cannot be established without additional sampling and detailed flow modeling. The fact that Calico Hills pore waters from depths as much as 100 m above the water table show evidence of hydrolysis reactions does suggest that perched waters are likely the dilute component.

Establishing bounds on the present and future compositions of perched waters and saturated-zone waters requires bounding the impact of the ion-exchange and hydrolysis reactions. Because zeolites in Yucca Mountain have relatively large selectivity coefficients for calcium and magnesium (Pabalan 1994; Viani and Bruto 1992), waters that percolate thru the zeolitized Tuff of Calico Hills will lose nearly all their calcium and magnesium before they reach the water table. This loss is evi-

dent in pore-water samples obtained from the lower part of Tuff of Calico Hills in drill holes UZ-14 and UZ-16 (Figs. 19 and 20).

As noted above, hydrolysis reactions that involve feldspar are limited by reaction affinity. That is, as the solution reaches saturation with a particular feldspar, the affinity for further reaction is progressively reduced until the solution is saturated with the feldspar, at which point the affinity for dissolution is zero. Therefore, the composition of waters in the devitrified units (such as the potential repository horizon) will be primarily constrained by saturation with feldspar and α -cristobalite. Pore waters percolating into the devitrified zones from non-welded units will already be supersaturated with feldspar and α -cristobalite as a result of glass dissolution reactions. Therefore, little additional dissolution is anticipated in the devitrified zones over-

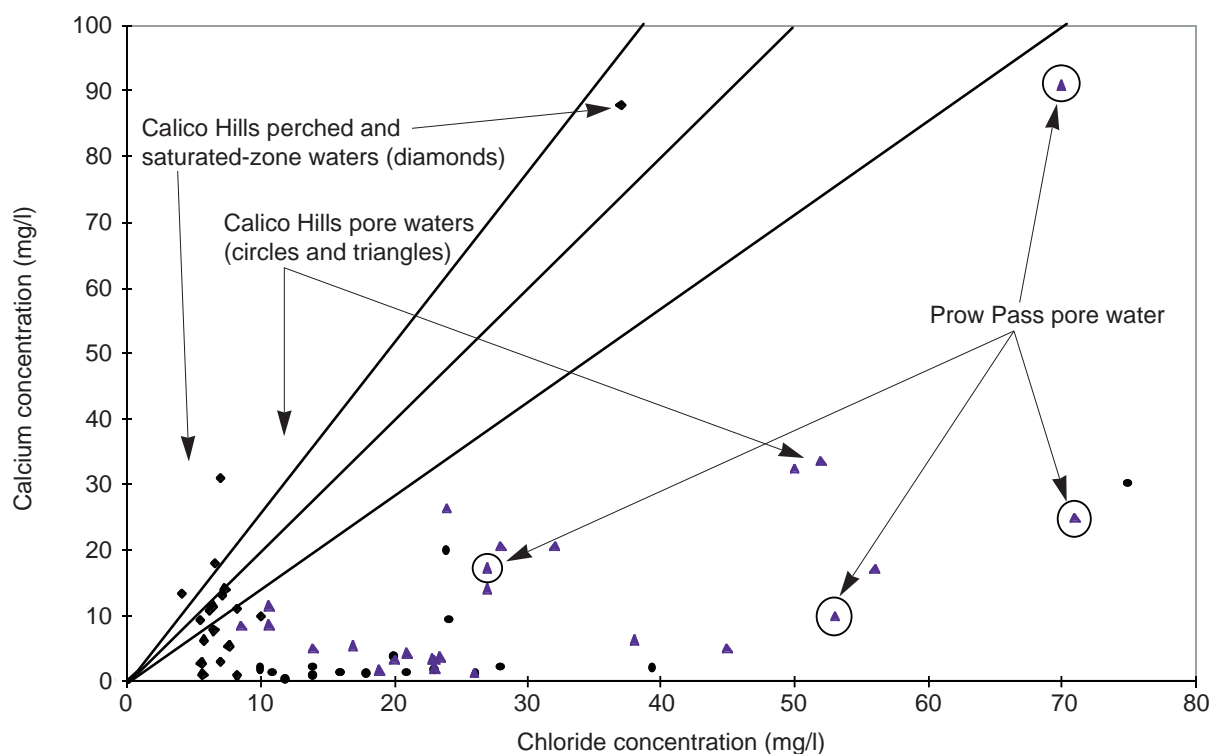


Figure 19. Calico Hills Calcium. The plot shows calcium versus chloride concentrations in Calico Hills pore waters, perched waters, and saturated-zone groundwaters. The straight lines are the regression fit and one-sigma deviations for calcium-versus-chloride precipitation data. (Drill-hole designations: circles: UZ-14; triangles: UZ-16; diamonds: saturated-zone waters.)

lain by nonwelded tuffs. In fact, soluble silica in pore waters from the nonwelded units may be crystallized onto existing α -cristobalite grains in the upper portion of the devitrified units, leading to reductions in porosity.

For vitric units, the situation is less straightforward because volcanic glasses cannot achieve thermodynamic equilibrium with an aqueous solution at ambient temperatures and pressures. That is, all volcanic glass would crystallize if it were not for the slow kinetics of nucleation and crystallization of the secondary phases that can form at ambient temperatures and pressures. Although the recrystallization of volcanic glass may be kinetically inhibited, glasses do dissolve at appreciable rates at ambient temperature and pressure when the dissolving waters are far from equilibrium with potential secondary phases. Many studies have been

carried out in recent years to gain an understanding of glass-alteration behavior, mainly to provide a basis for predictions of the alteration behavior of nuclear waste glasses. An important result of these short-term experimental studies is the finding that the glass dissolution rate is quite sensitive to the silica concentration in solution. As the silica concentration in solution approaches saturation with amorphous silica, the dissolution reaction slows down dramatically (Grambow 1992). Apparently, in order for glass alteration to proceed, the “gel reaction zone” that forms on the glass surface needs to dissolve. If the solution phase is near saturation with amorphous silica, the dissolution of this material is inhibited, presumably because the affinity of the dissolution reaction is low.

High silica activities in solution cannot be maintained very long (days to months) in the presence

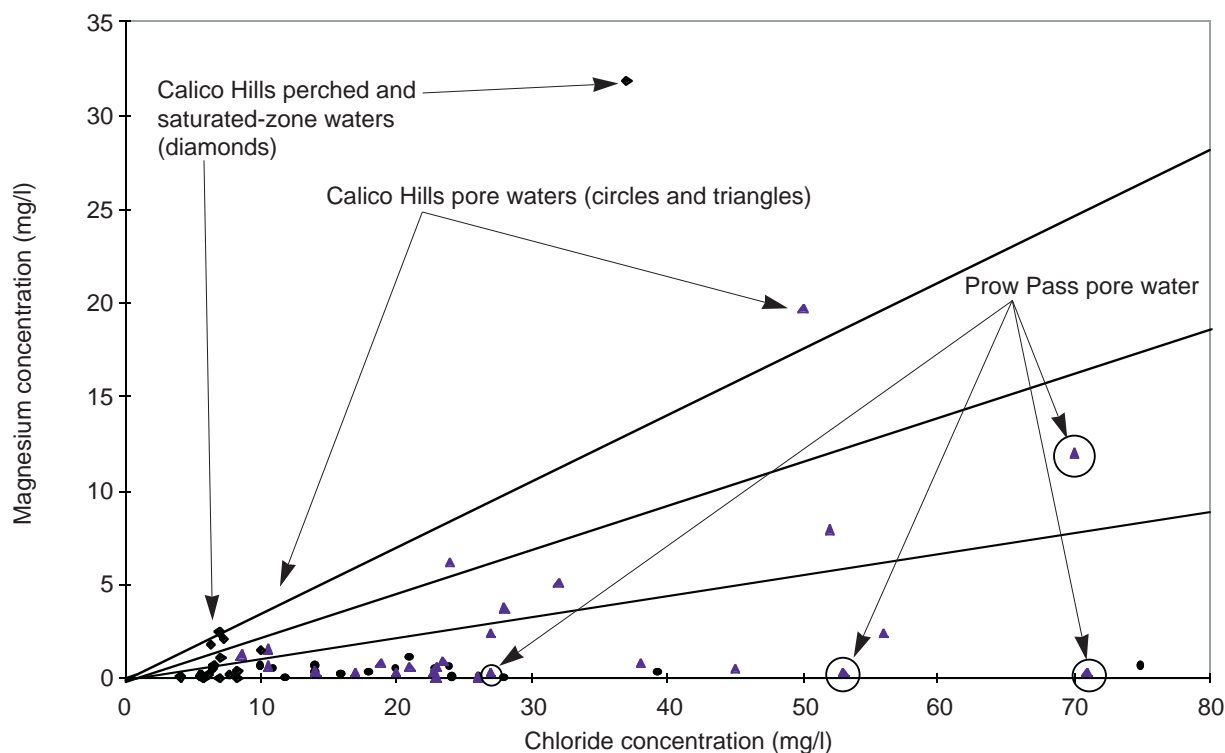


Figure 20. Calico Hills Magnesium. The plot shows magnesium versus chloride concentrations in Calico Hills pore waters, perched waters, and saturated-zone groundwaters. The straight lines are the regression fit and one-sigma deviations for magnesium-versus-chloride precipitation data. (Drill-hole designations: circles: UZ-14; triangles: UZ-16; diamonds: saturated-zone waters.)

of seed crystals of α -cristobalite and quartz (Rimstidt and Barnes 1980). This fact implies that Yucca Mountain waters with high silica activities lack sufficient surface areas of α -cristobalite or quartz seed crystals, in the units from which these waters were obtained, to control silica activities. This situation appears to be the case in nonwelded units within Yucca Mountain (Bish and Chipera 1989). The lack of adequate seed-crystal surface area most likely reflects the slow nucleation kinetics of these minerals at ambient temperature and pressure conditions (Nielsen 1964).

An important point is that most Yucca Mountain waters do not appear to be saturated with amorphous silica at ambient temperatures (Fig. 14). This observation suggests amorphous silica could not nucleate spontaneously, even in waters that contact volcanic glass. Interestingly, this does not mean that amorphous silica is not present in glassy samples. Iler (1973) has shown that the adsorption of ions such as Al^{3+} and Mg^{2+} onto the surface of amorphous silica greatly reduces the "equilibrium" solubility of this phase. Thus, amorphous silica could be a metastable phase in the vitric units, even though the silica concentrations measured in the waters of these units are below saturation levels with regard to amorphous silica. If adsorption of aluminum onto amorphous silica can lower the silica activity in solution, perhaps hydration and hydrolysis of (amorphous) silicic volcanic glass may produce the same result. The volcanic glass in the tuffs is initially 75 to 80 weight per cent SiO_2 and 12 to 13 weight per cent Al_2O_3 (Broxton et al. 1986). After hydration and hydrolysis ($\text{Na}^+ \leftrightarrow \text{H}^+$), the glass composition and structure likely approximate those of amorphous silica combined with some alumina and minor amounts of cations.

Whether or not such amorphous aluminosilicate material could maintain (metastable) equilibrium with an aqueous solution over time in the same manner that amorphous silica can is uncertain. The fact that volcanic glass remains abundant in many of the vitric units of Yucca Mountain (Bish et al. 1996b) after 11 to 13 million years in a hydrous

environment suggests that it can. However, this conclusion must be tempered by the observation that clay minerals are found in many, if not most, of these vitric units. The problem is that these clay minerals could have formed almost anytime in the 11-to-13-million-year interval since these units were deposited. Further, because the distribution of clays is not homogeneous in any given vitric unit, their origin must involve more than simply in-situ alteration in a hydrous environment; otherwise, all glasses in a given unit would show similar evidence of alteration. Open-system alteration may be a determinant of whether or not clays are formed (Gislason and Eugster 1987). For example, clays may be preferentially formed along pathways with higher than average water fluxes (Levy 1984). To model the long-term alteration behavior of silicic volcanic glass, particularly as a function of temperature, data on the kinetics of conversion of the glass to an amorphous aluminosilicate or clay would be required. Such data are unavailable at the present time.

However, data are available on the dissolution rates of silicic volcanic glasses. White et al. (1980) have presented rate constants for the dissolution of vitric silicic tuffs in distilled water at various pH values. The dissolution rate constants for individual elements indicate that the dissolution reactions are incongruent; that is, the dissolution rates of the individual elements were not directly a function of the concentration of the elements in the original glass. This fact suggests that an alteration layer was formed on the glass surface, which was enriched in silica, alumina, and potash relative to the original glass. This layer would presumably control the chemistry of waters in contact with it. It could be an amorphous aluminosilicate or an incipient clay. An important question is what would happen to this layer if temperatures were raised in the glassy units.

Knauss et al. (1986) reacted volcanic glass with J-13 water at 90°C for more than 2 months and found that no secondary minerals were produced and only minor etching was observed. This result suggests

the rate at which the water reacts with glass is very slow, even at somewhat elevated temperatures.

Unfortunately, without additional data on the nucleation and crystallization kinetics of the glass surface layer produced during alteration, reliable predictions of glass alteration behavior and the effect of glass alteration on water chemistry cannot be derived.

Hydrolysis reactions can have significant impacts on the pH of waters. The pH of waters in contact with the gas phase in pores in the unsaturated zone in Yucca Mountain will be buffered in the range from 6.8 to 8.0 depending on the actual partial pressure of carbon dioxide. The pH of groundwaters that become isolated from the carbon-dioxide reservoir in the unsaturated zone may increase as hydrolysis reactions consume hydrogen ions. The extent of such increases will be limited if the partial pressure of carbon dioxide in the saturated zone is buffered by some reservoir (for example, diffusion of gas from Paleozoic units). In any case, the potential increases in pH will be limited to values around 10, at which point silicic acid starts to dissociate, buffering the pH.

The oxidation-reduction potential, or Eh, of waters in contact with the unsaturated-zone gas phase will be oxidizing because this gas phase contains the same concentration of oxygen as the atmosphere (Yang et al. 1996). The range of Eh values to be expected in waters in the saturated zone is difficult to define because the identity of the dominant oxidation-reduction reaction is unknown at the present time. It could be reducing or oxidizing depending on the degree to which the waters have access to atmospheric oxygen or to reducing agents (for example, methane). The measurements reported by Ogard and Kerrisk (1984) suggest that reducing conditions exist at depth in some wells in the Yucca Mountain area. Why conditions are reducing in these wells is uncertain. Perhaps the wells access a volume of rock that is isolated from contact with the atmosphere and that contains sulfides or reduced organic compounds. Further measurements are required to develop a more complete understanding of oxidation-reduction potentials in

the saturated zone at Yucca Mountain.

In the absence of adequate glass-alteration models, some estimates of upper bounds on the concentrations of cations and bicarbonate species in perched waters, saturated-zone groundwaters, and Calico Hills pore waters can also be derived on the basis of data currently available for analyzed waters from aquifers in a variety of volcanic rock types at the Nevada Test Site (Ogard and Kerrisk 1984; Yang et al. 1988, 1996; McKinley et al. 1991). On the basis of the compilation by McKinley et al., the concentrations of major cationic constituents and bicarbonate in groundwater from Well UE-25 p#1 are at the high end of the range of concentrations reported for all waters (60 in all) sampled from volcanic units at the Nevada Test Site. In terms of the other anions, water from Well UE-25 p#1 is also at the high end of the range of chloride and fluoride concentrations. Sulfate, nitrate, and silica are exceptions. Sulfate is higher (449 mg/l) than UE-25 p#1 water only in Well J-11 in Jackass Flats. The elevated sulfate in this well may reflect the oxidation of sulfide minerals in the Wahmonie area to the east of the well. Nitrate is higher (up to 12 mg/l) in a number of wells, and silica is higher (up to 81 mg/l) in various wells. Well J-13 has nitrate and silica concentrations at the high end of the range of Nevada Test Site waters. In general, waters from Wells J-13 and UE-25 p#1 bound the range in concentrations of most of the major constituents found in waters from volcanic units over the entire Nevada Test Site.

Importantly, the Eh and pH of J-13 and UE-25p#1 waters do not bound the ranges for these parameters observed in waters from the Nevada Test Site. Both waters have a relatively oxidizing Eh (360–450 mV) and low pH (6.7–7.2). The pH values observed in Nevada Test Site waters from volcanic units range from 6.7 to 9.0 (McKinley et al. 1991). The range of Eh values in these waters is unknown as values for this parameter were not reported by McKinley et al. (1991). Ogard and Kerrisk (1984) report a range of –143 to +402 mV for groundwaters from the Yucca Mountain area.

C. SUMMARY AND CONCLUSIONS

The available data on the chemistry of pore waters, perched waters, and saturated-zone groundwaters at Yucca Mountain suggest there are essentially two types of waters at Yucca Mountain. Type-1 waters are found as pore water above Tuff of Calico Hills and from portions of Prow Pass member. Type-2 waters are found as perched water and saturated-zone groundwaters. The pore waters in Tuff of Calico Hills appear to be mixtures of these two water types.

Type-1 Waters

The chemistry of type-1 waters (mainly pore waters above Tuff of Calico Hills) will be controlled primarily by soil-zone processes, including evapotranspiration and the precipitation/dissolution of pedogenic minerals such as calcite, gypsum, and amorphous silica. The primary constraints on these processes are largely nonchemical and include evapotranspiration and the detailed soil-zone hydrology. These waters are generally saturated with opal-CT and do not appear to be influenced by hydrolysis reactions involving aluminosilicates.

Evapotranspiration is important in concentrating solutes in the soil zone that were originally in precipitation as wet-fall and dry-fall. Soil-zone hydrology controls the ionic strength and the chemical composition of waters infiltrating the unsaturated zone. Both the ionic-strength control and the compositional control reflect the flux and residence time of infiltrating waters in the soil zone prior to percolation into the unsaturated zone. The soil hydrology also impacts the water compositions through the crystallization sequence in which small pores are filled with early-formed phases, whereas the later-crystallizing phases preferentially form in the space available in the larger pores.

Because our understanding of soil-zone hydrology at Yucca Mountain is not fully developed, the impact of hydrology on the composition of unsaturated-zone pore waters can best be bounded by analyses of unsaturated-zone pore waters.

Fortunately, there is a trade-off between ionic strength and water volume. That is, the higher the ionic strength of the water (for example, more corrosive), the less of it there will be.

The pH and Eh of type-1 unsaturated-zone pore waters will be regulated by the composition of the gas phase in the pores. The Eh will be oxidizing (400–600 mV) because this gas phase has an oxygen partial pressure equal to that observed in the atmosphere (Thorstenson et al. 1989; Yang et al. 1996). The pH should remain in the range of 7 to 8 supported by carbon-dioxide partial pressures that are greater than atmospheric.

Type-2 Waters

The compositions of type-2 waters (perched and saturated-zone waters) are dominated by hydrolysis reactions. These reactions involve the exchange of cations (dominantly sodium) with hydrogen ions on the surfaces of aluminosilicate phases in the rocks (such as feldspar and volcanic glass). Hydrogen ions are supplied by the dissociation of carbonic acid. Therefore, the partial pressure of carbon dioxide is a critical parameter that controls hydrolysis reactions. It also has a major influence on the pH of the waters.

As we stated for type-1 waters, in systems open to the unsaturated-zone gas phase, the pH of the water will remain in the range of 7 to 8. Systems that become closed for some reason may have lower or higher pH values, depending on whether or not there are additional sources of carbon dioxide in the system. The upper bound on pH is approximately 10, the value at which silicic acid dissociation buffers the pH.

The Eh of type-2 water ranges from oxidizing to reducing, depending on whether the waters have access to atmospheric oxygen or to reducing agents, respectively.

Prediction of the future compositional variations in type-2 perched and saturated-zone groundwaters requires that the hydrolysis reactions be modeled. Such modeling requires knowledge of the secondary phases involved in the reactions.

For devitrified tuffs, these phases are likely dominated by alkali feldspar and α -cristobalite. Therefore, the future variations in the composition of waters in devitrified tuffs can be modeled by assuming saturation with alkali feldspar and α -cristobalite. The main unknowns in such modeling would be the pH and Eh of the system. The carbon-dioxide partial pressure must be known to calculate pH. Field measurements are required to constrain the Eh.

For glassy units, the modeling is more difficult because the identity of the secondary phases are not known with certainty. More importantly, the rates at which these phases form are unknown. There is information available on the rate of dissolution of silicic glasses. This information allows one to derive the initial chemistry of waters in vitric units, but it does not provide a basis for predictions of the long-term variations in water chemistry.

A Survey Approach

As a surrogate for the modeling approach, a survey of water chemistries in silicic volcanic rocks can be used to estimate bounds on the future variations of water chemistry in Yucca Mountain. A survey of water compositions from volcanic units indicates that waters from Wells J-13 and UE-25 p#1 have compositions that bound the observed range of variability for most major constituents. The main exceptions are pH, Eh, and chloride concentrations. Laboratory experiments designed to derive transport parameters, such as sorption coefficients and solubilities, have used these two water compositions and a range of pH values.

The variability in chloride concentrations is not a serious issue for the derivation of these parameters because chloride is not a strong complexing agent

for most radionuclides of interest. However, chloride concentrations in unsaturated-zone waters are important to the longevity of the waste package, as high chloride concentrations enhance corrosion rates.

Measurements of Eh in the saturated zone beneath Yucca Mountain suggest that reducing conditions exist locally. If redox conditions are generally reducing at depth in the saturated zone, the migration potential of radionuclides of elements such as neptunium and technetium would be greatly diminished. Additional field measurements at the site are required to test the variability in Eh and the redox state of saturated-zone groundwaters.

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